Kinematic Slowing of Molecules Formed by Reactive Collisions

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We report the generation of a beam of slow (translationally cold) KBr molecules formed by exoergic reactive collisions in counterpropagating beams of K atoms and HBr molecules. The intensity of the slow beam is estimated to $4 \times 10^{11}\ \mathrm{s}^{-1}\ \mathrm{sr}^{-1}$. The velocity distribution (density) peaks at 42.5 m/s corresponding to a formal temperature of 13 K. About 7% of the molecules move at velocities between 14.2 and 20 m/s and an estimated fraction of 7% is slower than 14.2 m/s.

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During the past decade techniques for cooling atoms have been developed and applied with great success to problems such as spatial confinement of atoms, high resolution spectroscopy, or Bose-Einstein-condensation. In an analogue cold molecule physics these topics are also of fundamental interest but, in addition, there is a wealth of specific molecular problems. Very promising is the wide field of cold chemistry, e.g., bimolecular reactive collisions at energies corresponding to temperatures in the low K and sub K region. While the higher range is useful for investigating molecule formation in cold interstellar clouds, the sub K range will provide access to a new chemistry where quantum phenomena become dominant and unknown effects await discovery [1–5]. Also confined gases of polar molecules are intriguing objects; the wide range, anisotropic dipole-dipole force dominates at low temperatures which may be useful in quantum computer schemes [6,7] or may lead to superfluidity and yet unknown collective properties [8,9]. The prerequisite for entering these fascinating fields of research is the availability of gases or beams of cold or slow (translationally cold) molecules. But, owing to the more complex electronic and geometric structure, the well-established techniques for cooling atoms are not applicable to molecules and new methods have to be found. To date, a variety of such cooling or slowing methods is already available; for detailed descriptions we refer to a recent review article by Doyle and coworkers [10].

In this Letter we present another technique for the preparation of slow (translationally cold) molecules and report first experimental results. It is applicable to metal (Me)-halogen (X) molecules MeX, whose extremely large electric dipole moments up to $10D$ make them an ideal object for investigations of cold dipolar gases and for experiments on guiding and trapping at moderately strong inhomogeneous electrostatic fields. In addition, the chemical reactivity of these molecules allows an easy access to the field of cold chemistry. Candidates for studies of reactive processes are bimolecular metal exchange collisions where, for example, a beam of slow MeX molecules interacts with a gas of ultracold alkali or alkali-earth atoms confined in a magneto-optical trap (beam-gas arrangement) and the metal atoms are exchanged.

The slow salt molecules MeX are formed in a reactive collision of the type $\mathrm{Me} + \mathrm{HX} \rightarrow \mathrm{MeX} + \mathrm{H}$, where the extremely small ratio of the product masses $m_{\mathrm{H}}/m_{\mathrm{MeX}}$ is an essential prerequisite for the slowness of the salt molecules. This is readily understood if one considers first the collision in a coordinate frame that is fixed to the center-of-mass of the colliding particles (c.m. frame). Since by definition the sum of the momenta of the interacting particles vanishes in this frame at all times, the relation

$$\mathbf{u}_{\mathrm{MeX}} = -\frac{m_{\mathrm{H}}}{m_{\mathrm{MeX}}}\mathbf{u}_{\mathrm{H}} \qquad (1)$$

between the final velocities of the products holds, indicating that the velocity of the heavy salt molecules, $\mathbf{u}_{\mathrm{MeX}}$, is by the crucial mass factor $m_{\mathrm{H}}/m_{\mathrm{MeX}}$ smaller than the one of the light H atom, $-\mathbf{u}_{\mathrm{H}}$.

The magnitude of the speeds results from the total energy available to the products E_{tot} given by the sum of the mean translational and internal (vibrational and rotational) energies of the approaching particles and the energy ΔD_0^0 released during the reaction

$$E_{\mathrm{tot}} = E_{\mathrm{tr}} + E_{\mathrm{int}} - \Delta D_0^0. \qquad (2)$$

After the collision, E_{tot} is partitioned among the translational and internal degrees of freedom of the products. The maximal speed of the separating products results when E_{tot} is completely transferred into the translational degree of freedom; for MeX it is

$$u_{\mathrm{max,MeX}} = \frac{m_{\mathrm{H}}}{m_{\mathrm{H}} + m_{\mathrm{MeX}}} 1414\sqrt{E_{\mathrm{tot}}/(\mathrm{kJ/mol})}\ \mathrm{m/s}. \qquad (3)$$

Typically, E_{tot} and m_{MeX} are around 28 kJ/mol and 100 amu, respectively, providing an upper limit of around 74 m/s. However, a significant fraction of E_{tot} is, in general, transferred into the internal degrees of freedom of MeX leading to velocities below the upper limit. Detailed experimental data are available for Ba + HI [11]; in the average about 90% of E_{tot} is channeled here into internal energy where high vibrational energies are associated with low rotational energies and vice versa. In the extreme case that the molecules absorb all available energy, MeX would even come to a standstill with respect to the c.m. For endoergic reactions ($\Delta D_0^0 > 0$) E_{tot} is typically below 28 kJ/mol and $u_{\max,\text{MeX}}$ may become very slow if the sum of initial energies of the reagents exceeds ΔD_0^0 only slightly.

In the laboratory (LAB frame) the c.m. is, in general, not at rest but travels with the velocity

$$\mathbf{C} = \frac{m_{\text{Me}}\mathbf{V}_{\text{Me}} + m_{\text{HX}}\mathbf{V}_{\text{HX}}}{m_{\text{Me}} + m_{\text{HX}}}, \tag{4}$$

where $\mathbf{V}_{\text{Me}}$ and $\mathbf{V}_{\text{HX}}$ are the velocities of the indicated particles. With respect to the LAB frame, the salt molecules move then with the velocity

$$\mathbf{V}_{\text{MeX}} = \mathbf{C} + \mathbf{u}_{\text{MeX}} \tag{5}$$

and a molecule even standing still in the c.m. frame ($u_{\text{MeX}} = 0$) may move rapidly in the laboratory. So, at first glance, the motion of the center-of-mass appears to prevent a formation of slow molecules by chemical reaction. But there is a simple remedy: if one chooses the collision kinematics such that C becomes small, preferentially zero, the LAB and c.m. frame nearly coincide and the MeX molecules are slow in both frames (kinematic slowing). According to Eq. (4) $C = 0$ holds if (a) the velocities of Me and HX point into opposite directions and (b) the ratio of reagent speeds is equal to the inverse ratio of their masses.

In our experiment we have approached these conditions by (a) preparing two overlapping counterpropagating reagent beams whose most probable speeds are tuned such that their ratio of magnitudes approximately assumes (b) $V_{\text{Me}}/V_{\text{HX}} = m_{\text{HX}}/m_{\text{Me}}$. For a first experimental demonstration of this concept we selected the reaction $\text{K} + \text{HBr} \rightarrow \text{KBr} + \text{H}$. This process is exoergic by $\Delta D_0^0 = -24 \pm 10$ kJ/mol [12]. It is particularly suited for this experimental demonstration because velocity matching required by condition (b) is sufficiently well fulfilled at the usual operational conditions of the two beam sources used. Alkali reactions of this type have played an important role in the history of molecular reaction dynamics and many properties are known such as absolute integral reaction cross sections [13], or product rotational energy [14] and angular and velocity distributions [15].

A schematic diagram of the molecular beam apparatus is shown in Fig. 1. The pulsed valve creates a short (600 μs) HBr beam pulse that passes a skimmer and the liquid N_2 cooled aperture for collimation. The continuous K beam expands through a small orifice in the front chamber of the K oven whose rear chamber contains a few grams of the metal. The chambers are heated to 1050 K (front) and 770 K (rear). The beam is collimated by a skimmer and the heated aperture. Oven and skimmer are mounted within a water-cooled Cu-housing. The liquid N_2 cooled Cu plates A and B are cold traps to reduce the background pressure of the alkali vapor. The beams are aligned optically to guarantee counterpropagation and full overlap.

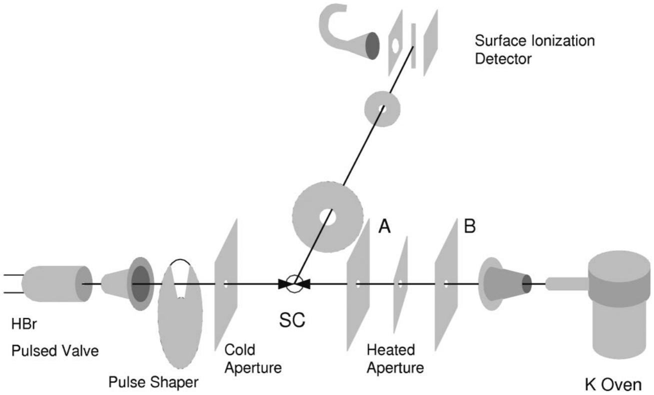

FIG. 1. Schematic diagram of the counterpropagating molecular beams arrangement. For details see text.

In the counterpropagating beam arrangement collisions between the reagent particles take place over the entire length of the overlap volume with a maximal rate around the scattering center (SC) between the two sources. In the course of such collisions two different processes occur forming either the products KBr and H (reactive scattering) or K and HBr (nonreactive scattering). Both product species, K and KBr are detected by surface ionization on the hot surface of a Re ribbon. The impinging K and KBr desorb quickly (the residence time is $\ll 1$ ms) as K^+ ions. The open channeltron electron multiplier converts the ions to electron pulses which are amplified and finally counted by a multichannel analyzer (MCA). The two apertures between SC and the ribbon select products that are formed in a small volume around SC and scattered by a mean angle of 90° with respect to the common beam axis. The ribbon, the multiplier, and the two apertures are housed in a separately pumped vacuum chamber maintained at a pressure of $<10^{-7}$ mbar. The low pressure is essential for avoiding excessive scattering of the slow molecules by the residual gas particles while they approach the Re ribbon.

The velocity distribution of the scattered particles is measured directly using the conventional time-of-flight (TOF) technique. In principle, the HBr beam pulse creates a short pulse of products that enters the detector chamber and spreads on its way to the ribbon according to the velocity distribution of the particles. The fast ones reach the ribbon first and the signal pulses are allocated to the first channels of the MCA, while the slow ones require a considerably longer TOF and their signal is allocated to large channel numbers. Measuring cycle and repetition frequency are controlled by a disk equipped with one broad slit (pulse shaper) rotating at 40 Hz in front of the HBr skimmer. Per revolution it creates optically a trigger pulse that energizes the valve just in time for the beam pulse to pass the moving slit freely. By this, the shape of the beam pulse and the instant of time its center passes the slit are precisely known. The velocity of a particle X whose signal pulse is allocated to channel N of the MCA is then

$$V_X = S/(t_N - \tau_0), \tag{6}$$

where $S = 259$ mm is the distance between SC and the ribbon (length of the flight path), t_N the time of arrival allocated to channel N, and τ_0 the time the center of the beam pulse arrives at SC (all times refer to the valve trigger pulse as time zero).

The velocity distributions of the two beams are measured in an analogous way (devices are not shown in Fig. 1). For this purpose the complete metal beam source is shifted on rails perpendicular to the beam axis until both beams spread freely. In this ''off axis'' position the K beam is chopped by a slotted (two slits 0.3 mm wide) disk rotating at 232 Hz and detected by a surface ionizer mounted 260 mm further downstream. The HBr beam pulses are detected by a mass spectrometer whose electron impact ionizer is located 1960 mm downstream from the valve. We determined for the K and HBr beams most probable velocities of 818 ± 30 m/s and 450 ± 6 m/s and a full width at half maximum of the distributions of ± 450 m/s and $\pm < 50$ m/s, respectively. The ratio of these most probable velocities does not exactly fulfill condition (b). But this has no serious consequences because the broad K velocity distribution provides for every velocity of the narrow HBr distribution an exactly matched velocity at nearly peak intensity.

From these two beam velocities we calculated a mean relative translational energy of the colliding particles of $E_{\rm tr} = 21 \pm 1$ kJ/mol. Because of the low temperature of the pulsed valve (290 K) and the complete relaxation of the internal degrees of freedom of the expanding gas, the internal energy of the HBr beam is negligible and one obtains for the total available energy [Eq. (2)] $E_{\rm tot} = 45 \pm 11$ kJ/mol. Energy conservation predicts then a maximal velocity of KBr [Eq. (3)] $u_{\rm max,KBr} = 79 \pm 9$ m/s, where the bandwidth reflects the error margins of ΔD_0^0 and $E_{\rm tr}$.

The experimental results are shown in Fig. 2. Plotted is the intensity of the scattering signal (counts per time channel N) versus t_N. The full squares represent the TOF distribution of scattered particles for K + HBr It is characterized by a narrow peak at short times where we expect the signal for elastic scattered K atoms and a conspicuous, intense and broad peak at larger times which extends clearly to 10 ms. The continuation of the gradually declining slope is shown in the inset that displays a sliding average of the intensity over 10 time channels on a larger scale. The data indicate a weak, but significant signal up to 19 ms. We associate this peak and the extended slope with the anticipated flux of the slow KBr product molecules. For comparison we have replaced HBr by Kr and studied also the pure elastic scattering process K + Kr. The TOF distribution (open triangles) exhibits, as expected, only the sharp peak of elastically scattered K atoms which levels off quickly toward larger times without any trace of a second peak.

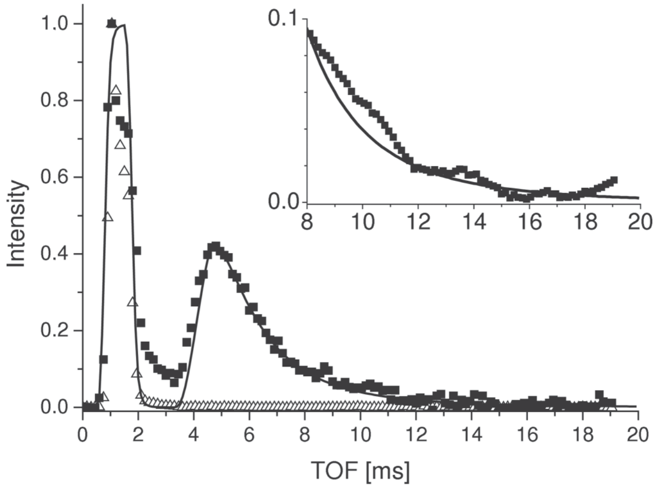

FIG. 2. Measured time-of-flight (TOF) distributions of scattered particles. The full squares represent the results for K + HBr. The narrow peak at small times is associated with elastic scattered K atoms, while the broad peak at large times is caused by the slow reaction products KBr. The inset shows a sliding average over 10 channels on a magnified scale. For comparison, the results for K + Kr (open triangles) exhibit only the narrow peak of the elastic scattering. The solid line is a numerical simulation.

The solid line in Fig. 2 is the result of a numerical simulation which includes the known beam velocity distributions and the temporal shape of the HBr or Kr beam pulse (shutter function). The elastic peaks reflect only the scattering kinematics and are used to determine width and center τ_0 of the shutter function; we find a width of 0.95 ms and $\tau_0 = 1.05$ ms. On the other hand, the shape of the broad peak is dominated by the dynamics of the reactive process and incorporates the KBr velocity distribution. To extract this information we describe the product flux velocity distribution by a simple parameterized function and vary the free parameters until the simulated and measured data agree. We have chosen the expression

$$f(V) = \begin{cases} \text{const} \times (V_0 - V)V^q & \text{for } 0 \leq V \leq V_0 \\ 0 & \text{for } V > V_0 \end{cases} \tag{7}$$

that is sufficiently flexible to describe typical features, such as a peak and a gradual descent to zero toward both $V = 0$ and the largest velocity V_0, with the aid of only two parameters, V_0 and q.

The best simulation of the broad peak and the extended slope was obtained for $V_0 = 85$ m/s and $q = 2.0$. The corresponding flux velocity distribution of the KBr molecules (dashed curve) and the density distribution (solid line) are displayed in Fig. 3. The curves feature a maximum at the most probable velocities $V_{\rm mp} = 56.7$ m/s (flux) and

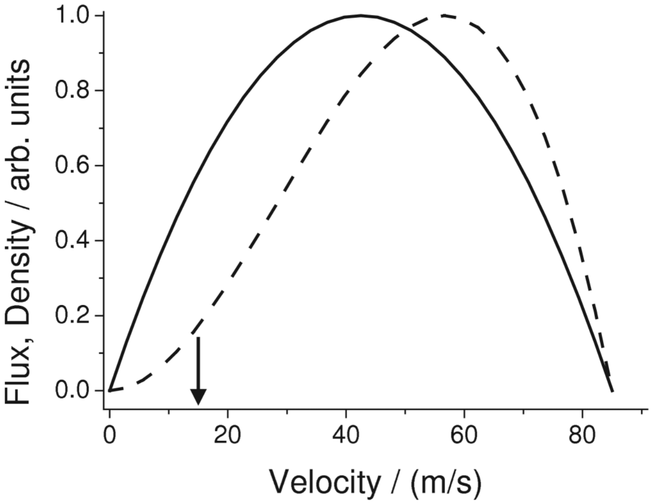

FIG. 3. Best fit flux (dashed line) and density (solid line) velocity distributions of KBr. The peak velocities correspond to formal temperatures of 13 (density) and 15 K (flux). The arrow marks the smallest velocity accessible to our setup.

42.5 m/s (density). Although the distributions are extremely nonthermal we compare as usual V_{mp} with the corresponding quantity of a Maxwellian distribution and obtain a formal temperature of 13 K (density) and 15 K (flux). The low velocity slopes of these distributions determine directly the shape of the extended slope of the simulated curve shown in the inset of Fig. 2. The good agreement with the data allows us to deduce the fraction of slow molecules from the density distribution at least down to the experimental limit of $V = 14.2$ m/s (marked by an arrow). We find that about 7% of the molecules move at velocities between 14.2 and 20 m/s, and, considering also the extrapolated section of the curve ($V < 14.2$ m/s), that 7% are slower than 14.2 m/s.

Based on the estimated number densities of the beams at SC of 10^{10} cm^{-3} (K) and 10^{13} cm^{-3} (HBr), the volume of SC of 0.1 cm^3, the most probable relative velocity 1268 m/s, and the differential reaction cross section 3×10^{-16} cm^2 sr^{-1} [13] we obtain an intensity of the slow molecules of about 4×10^{11} s^{-1} sr^{-1}. However, using pulsed metal beam sources (e.g., the laser ablation technique) and optimizing the HBr jet expansion conditions an enhancement by a factor of 10^3 to 10^4 is practicable. The application of such an intense beam in future beam-gas experiments on cold reactive scattering processes looks promising. Many experiments in physics and chemistry involving cold particles require their spatial confinement within so-called traps. Atoms are confined by a now standard procedure using magneto-optical forces whose dissipative nature allows us also to load the trap continuously with atoms entering the device from the outside. In the case of molecules only electric or magnetic forces [10,16,17] have been used so far but their conservative nature excludes a continuous loading from the outside. However, if the molecules are created within the force field of the trap, continuous loading would be possible. And exactly this can be achieved using the counterpropagating beams arrangement. By allowing the beams to pass the trap, molecules are created inside the force field by reactive collisions and, provided they are sufficiently slow and attracted to the field's center, they are confined and accumulate in the trap until the rates of gain and loss are equal. Experiments on trapping in two (guiding) and three dimensions are in progress.

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